Adsorption 11: 397–401, 2005

Simulated Water Adsorption Isotherms in Hydrophilic and Hydrophobic Cylindrical Nanopores

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Abstract. Grand canonical Monte Carlo simulations are performed to study the adsorption of water in single-walled carbon nanotubes (SWCNs). At room temperature the resulting adsorption isotherms in (10:10) and wider SWCNs are characterized by negligible amount of water uptake at low pressures, sudden and complete pore filling once a threshold pressure is reached, and wide adsorption/desorption hysteresis loops. The width of these loops decreases as pore diameter narrows. Adsorption/desorption hysteresis loops are not observed for water adsorption in (6:6) SWCNs. When the nanotubes are doped with small amounts of oxygenated sites it is possible to obtain adsorption isotherms in which the water uptake increases gradually as the pressure increases. Simulated X-ray diffraction patterns for confined water are also reported.

Keywords: SPC/E water, grand canonical Monte Carlo simulations, Debye-functional analysis, XRD pattern

1. Introduction

Carbon nanotubes were first obtained by Iijima (1991) and several methods are now available for their production (Ebbesen, 2000). Theoretical studies predicted that single-walled carbon nanotubes (SWCNs) can be used as storage devices for hydrogen (Lueking and Yang, 2003), may enhance chemical reactions (Halls and Schlegel, 2002), and could be used as sensors (Zhao et al., 2002). In these and other applications the presence of water vapor could compromise the performance of the nanotubes. Thus, it is crucial to be able to understand and predict the thermodynamic behavior of water confined within SWCNs.

Water adsorption in carbons is known to be strongly affected by the presence and density of oxygenated groups on the carbon surface (Müller et al., 1996; Müller and Gubbins, 1998; McCallum et al., 1999; Brennan et al., 2001). In the absence of such groups, the adsorption of water is insignificant at pressures below the capillary-condensation pressure, and it is usually accompanied by large adsorption/desorption

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hysteresis loops (Rudisill et al., 1992). As the surface density of oxygenated groups increases, water adsorption occurs at increasingly lower pressures, and as pressure is increased a continuous pore filling may occur. Recently Jorge et al. (2002) showed that the location and density of oxygenated sites within carbon-slit pores can significantly alter the simulated adsorption isotherms and the calculated Henry constants. Recent experimental data were reported by Bekyarova et al. (2002), who found that water can be adsorbed within hydrophobic nanohorns at pressures below saturation, and by Maniwa et al. (2002), who observed an ordered structure for water confined in (10:10) SWCNs at temperatures below 235 K. That structure resembles the one predicted via molecular dynamics by Koga et al. (2001). Other molecular simulation studies include, but are not limited to, those of Martí and Gordillo (2002), who calculated the diffusion coefficients of confined supercritical water; Brovchenko et al. (2001, 2003), who found that when water is confined in a hydrophobic cylindrical pore the diffusion along the pore axis is faster than the bulk self diffusion and that the vapor-liquid hysteresis critical temperature for confined water can be 200 K lower than that of bulk water; Hummer et al. (2001), who studied the flux of water molecules through short SWCNs.

Our group has been studying the adsorption of water in carbon-slit pores and in doped and un-doped SWCNs in a wide temperature range (Striolo et al., 2003, 2004a, 2004b, 2004c). Our results provide an extensive data set for adsorption isotherms as a function of pore width and morphology, as well as a detailed investigation on the effect of temperature and chemical heterogeneity on thermodynamic, structural, and transport properties of confined water. We also provide details on the mechanism of adsorption and desorption with the aid of a large number of intermediate configurational snapshots. Here we briefly summarize our results for the adsorption of water in SWCNs of several diameters at 298 K. The SWCNs are in some cases doped with small amounts of oxygenated sites, modeled as carbonyl groups. To further characterize the properties of confined water we report simulated X-ray diffraction patterns for confined water and representative configurational snapshots. The results presented here complement earlier investigations on the effect of pore blocking and connectivity on the adsorption of water in carbons (Brennan et al., 2002), and those for the adsorption of vapor-methane mixtures on activated carbons (Müller et al., 2000).

2. Simulation Details

The diameters of (6:6), (10:10), (12:12), and (20:20) SWCNs, based on the distance between carbon-atom centers on opposite sides of the SWCN, are 0.81, 1.36, 1.63, and 2.71 nm, respectively. Periodic boundary conditions are implemented along the pore axis so that the pores are effectively infinitely long. No water is allowed outside the nanotubes, thus the pores should be imagined as surrounded by vacuum. The SPC/E model (Berendsen et al., 1987) was chosen to describe the water molecules. Each carbon atom in the system is represented as a Lennard-Jones sphere whose interaction parameters were taken from Steele (1974). High-energy oxygenated groups are modeled as carbonyl groups (C=O). The oxygen atom in the carbonyl group is modeled as a Lennard-Jones sphere with a point charge at its center. The Lennard-Jones parameters were taken from the OPLS parameterization (Jorgensen and Swenson, 1985). The Lennard-Jones parameters for the unlike interactions are obtained by the Lorentz-Berthelot combining rules. In Fig. 1 schematic representations of un-doped and doped SWCNs are reported. Oxygenated groups are either concentrated in a narrow section along the nanotube, or randomly placed on the porous surface.

The grand canonical Monte Carlo (GCMC) method was used to simulate water adsorption. For the adsorption path of the isotherms the pores were first

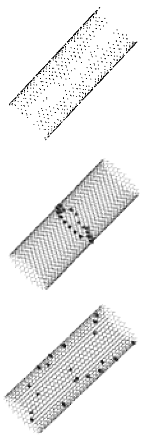

Figure 1. Schematic representation of (20:20) SWCNs. From top to bottom the sketches represent one un-doped SWCN, one doped SWCN with carbonyl groups concentrated in a narrow section along the nanotube axis, and one doped SWCN in which the carbonyl groups are randomly placed on the porous surface.

considered empty. Simulation runs were performed at increasing chemical potentials. Desorption cycles were initiated with a typical configuration of a filled pore and the chemical potential was reduced until the pores were emptied from previously confined water. The amount of adsorbed water, as a function of pressure, is reported in terms of surface coverage, ξ, defined as the number of adsorbed water molecules per square nanometer of porous surface. Further details can be found in our earlier publications (Striolo et al., 2003, 2004a).

Following Gnutzmann and Vogel (1990), the structure of confined water for selected systems was characterized by the use of the Debye function:

$$I(b) = \sum_{n} \sum_{m} f_n(b) f_m(b)[\sin(2\pi b r_{nm})]/(2\pi b r_{nm}). \tag{1}$$

In Eq. (1) the intensity I of the diffracted coherent radiation is a function of the length of the vector in reciprocal space ($b = 2\sin\theta/\lambda$), λ is the wavelength of the incident light, θ is the Bragg angle, r_{nm} is the separation between atoms n and m. The functions $f_n(b)$ and $f_m(b)$ are the atomic scattering amplitudes for the atoms n and m. Only the positions of confined oxygen atoms were used. Values for the atomic scattering amplitudes were obtained from Cromer and Mann (1968). The wavelength of the incident light was considered equal to that of synchrotron radiation (0.10 nm).

3. Results and Discussion

In Fig. 2(A) we report the simulated adsorption isotherms for water in (6:6), (10:10), (12:12), and (20:20) SWCNs at 298 K. Adsorption isotherms simulated in (10:10), (12:12), and (20:20) SWCNs are of type V, characterized by negligible water uptake at low pressures, sudden and complete pore filling once a threshold pressure is reached, and wide adsorption/desorption hysteresis loops. No hysteresis can be observed for water adsorption in (6:6) SWCNs at this temperature, and the amount of water adsorbed increases gradually as the pressure increases. The capillary-condensation pressure and the width of the adsorption/desorption hysteresis loops decrease with decreasing pore diameter for (10:10) and larger SWCNs.

In Fig. 2(B) we report the isosteric heat of adsorption at low coverage, q_{st}, for water adsorbed in (6:6), (10:10), (12:12), and (20:20) SWCNs. At low coverage q_{st} increases as pore diameter decreases. Considering that large positive values for q_{st} indicate strong attractions between the pore and one water molecule, our results suggest that when the pore diameter decreases pore-water interactions become more attractive. It is instructive to note that q_{st} increases much more slowly as the surface coverage increases for water adsorbed in (6:6) SWCNs than for water adsorbed in wider SWCNs. This result is a consequence of the small diameter of (6:6) SWCNs: the first adsorbed water molecules cannot establish hydrogen bonds with other water molecules in such a narrow pore, and predominantly pore-water interactions are responsible for attracting additional water molecules within the pore.

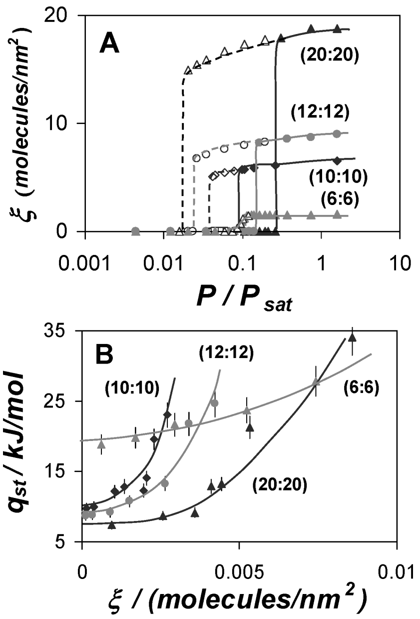

Figure 2. Simulated adsorption isotherms (A) and isosteric heat of adsorption at low coverages (B) for water in undoped SWCNs at 298 K.

In Fig. 3 we report simulated adsorption isotherms for water in (10:10) SWCNs doped with small numbers of carbonyl groups. Our results show that when carbonyl groups are present on the porous surface, the SWCNs fill at lower pressures than when no carbonyl groups are present and that the width of the adsorption-desorption hysteresis loops is narrower. Our results also indicate that when the carbonyl groups are concentrated in a narrow section along the nanopore axis, the amount of water adsorbed increases gradually as the pressure increases. The gradual water uptake is due to the formation of a cluster of water molecules in correspondence to the carbonyl groups at low pressures. As the

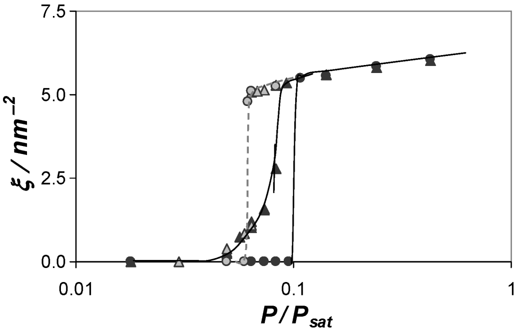

Figure 3. Simulated adsorption isotherms for water adsorbed in (10:10) SWCNs at 298 K. The SWCNs are doped with 0.318 carbonyl groups per square nanometer of porous surface. Results are shown when the carbonyl groups are randomly displaced along the nanopores (circles), and when they are concentrated in a narrow section along the nanopores axis (triangles). Black symbols are for adsorption, grey for desorption. Lines are guides to the eye.

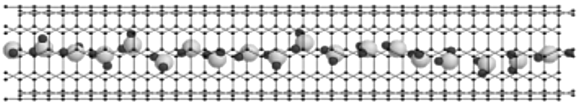

Figure 4. Representative snapshot for water confined in (6:6) SWCNs at 298 K.

pressure increases, the cluster grows in size until the pores are completely filled with water. When the carbonyl groups are randomly displaced on the porous surface or when the nanotubes are larger than (12:12) SWCNs, this mechanism was not observed and type V adsorption isotherms were obtained in all cases considered (results not shown here for brevity).

In Fig. 4 we report one representative configurational snapshot obtained for water confined in (6:6) SWCNs at 298 K. Visual analysis of this snapshot confirms that water confined in such narrow cylindrical pores forms a one-dimensional chain-like structure in which each water molecule donates one hydrogen atom to one next neighbor, receives one hydrogen atom from the other neighbor, and maintains the remaining hydrogen atom dangling towards the carbon surface. This configuration reproduces the features observed by Mashl et al. (2003) and those computed by Hummer et al. (2001) and by Mann and Halls (2003).

To allow the comparison between simulation and available experimental results, we simulated the X-ray diffraction pattern for water confined in (10:10) SWCNs at 248 K. The simulated patterns are shown in Fig. 5 where available experimental data from Maniwa et al. (2002) are also reported for comparison. Simulated X-ray diffraction patterns indicate a narrow but intensive peak at $Q = 22\ \text{nm}^{-1}$, in agreement with experimental observations. Our results indicate that water confined in (10:10) SWCNs at 248 K is an octagonal water nanotube, as suggested by experimental results.

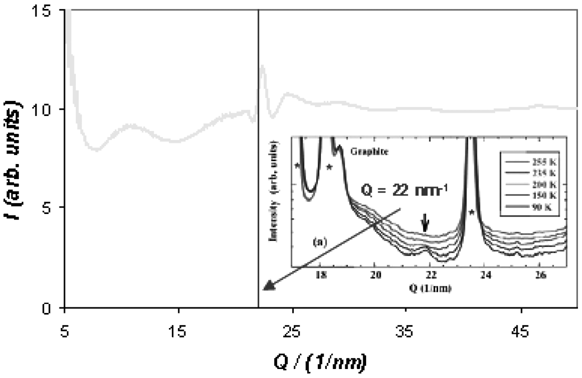

Figure 5. Simulated and experimental X-ray diffraction patterns for water confined in (10:10) SWCNs. Simulated results are for confined water at 248 K. Experimental data were obtained at different temperatures (see inset taken from Maniwa et al., 2002), and indicate that a peak at $Q = 22\ \text{nm}^{-1}$ grows at temperatures below 235 K. The symbols * denote diffractive peaks that are typical for bulk ice or graphite. Q is the amplitude of the scattering vector $Q = 4\pi \sin\theta/\lambda$ (see Eq. (1)).

Acknowledgments

This work was partially supported by the US Department of Energy under Contract No. DE-FG02-98ER14847 and Contract No. DE-FG05-94ER14421. The authors acknowledge generous allocations of computing time by NPACI, San Diego, and NERSC, Berkeley.

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